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AN INVESTIGATION OF FACTORS RELATED TO THE OCCURRENCE OF MANGANESE IN NATURAL STREAM WATERS

A Thesis

Presented to

The Faculty of the Graduate Division

by

Thomas Robert McWhorter

In Partial Fulfillment

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AN INVESTIGATION OF FACTORS RELATED TO THE OCCURRENCE OF MANGANESE IN NATURAL STREAM WATERS

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SUMMARY

Manganese is a common ingredient in many natural waters throughout the United States. The appearance of manganese in greater than trace quantities has created many problems in the field of water purification. Domestic and industrial water users raise objections to the presence of manganese in finished waters. The removal of manganese can be extremely difficult and unreliable by low-cost treatment methods, since manganese will pass through many types of treatment plants.

The occurrence of manganese in natural waters is of a seasonal nature and often unpredictable. Little correlation exists between geological manifestations of manganese on water sheds and its occurrence in rivers, streams, lakes, and underground water supplies. Manganese is becoming increasingly significant in water treatment since it is frequently present in large power, flood control, or water supply reservoirs developed to increase water resources.

Although some theories have been advanced, the actual mechanism of manganese reduction and its occurrence in natural waters is not clearly defined. This investigation was, therefore, undertaken to determine factors related to the changes causing the seasonal occurrence of soluble manganous manganese in natural waters. These factors were determined by physical and chemical analysis and observations of a small unpolluted spring and its stream.

Seasonal and diurnal variation of dissolved oxygen, pH, manganese, iron, alkalinity, carbon dioxide, and temperature were observed in the spring waters. Physical and chemical variations of water quality along the course of the stream bed were also observed. Limited microscopic examinations were made throughout the study.

Manganese was found to be absent from the spring water during the winter, to occur in low concentrations in the early spring and in high concentrations throughout the summer. Iron bacteria, Leptothrix ochracea, were found present with the manganese in the spring waters and were found to be associated with the rapid removal of manganese in the stream waters containing dissolved oxygen.

The occurrence of manganese in the spring waters was found to be related to temperature, dissolved oxygen and iron. Temperature was related to the occurrence of manganese through its effect on biological activity and dissolved oxygen. The absence of dissolved oxygen was closely related to the presence of high concentrations of manganese. The presence of Leptothrix ochracea in the stream waters containing manganese and dissolved oxygen caused a rapid reduction in the concentration of soluble manganese.

CHAPTER I

INTRODUCTION

Manganese is a common ingredient, to a lesser or greater degree, in nearly all natural waters throughout the United States. While plant life is dependent on trace quantities of this element as an activator of enzyme systems, the appearance of manganese in greater than trace quantities has created many problems in the field of water purification. Domestic and industrial water users raise many and varied objections to to the presence of manganese in finished waters depending on their particular use for the water and the concentration of manganese present. The presence of iron is generally associated with that of manganese and, more often, in greater quantities. The tolerable amount of manganese is dependent on water use; some industries may require manganese-free water, while others may tolerate manganese with no deleterious effects. The United States Public Health Service recommends a maximum of 0.05 milligrams per liter (mg/l) of manganese in water to be used for interstate commerce.[1] It has been suggested that a better limit would be the presence of no manganese.[2]

Among the industries requiring low limits for iron and manganese are soft drinks, brewing, confectionary, ice manufacturing, laundering, plastics, textiles, and pulp and paper industries. Manganese and iron are readily absorbed by pulp fibers causing a loss of brightness from iron and visible blackish mottling from manganese. Textile fibers are

affected in much the same way. The taste of beverages is impaired by iron and manganese. Domestic users of waters containing these elements find they stain plumbing fixtures, give laundered goods a dull brownish or grayish color, impair the taste of water beverages, and may give the water itself a turbid appearance. At water treatment plants, the filter sand may become coated with black manganic oxide and may grow in size,[3] particularly if the manganese is tied up in organic complexes. Length of filter runs may be markedly shortened and, unless backwashing is sufficient, the sand may become cemented into small ball-like masses. Manganese and iron can build up in the distribution system and constrict flow. Manganese may adhere to iron and copper pipe walls, concrete, and other surfaces in a highly crystalline form, thus having an auto-catalytic effect for further crystal growth.[3] Pipe capacity may be restricted by the growth of a black slime of crenothrix-type organisms which remove manganese from solution and deposit it on the pipe interior.[2]

The occurrence of manganese in natural water is of a seasonal nature and often unpredictable. Removal of manganese is extremely difficult and unreliable by low-cost treatment methods. The suddenness and severity of the occurrences often force industrial and domestic users to resort to costly remedial measures; industries are at times forced to shut down plant operations.

While iron may be removed by simple oxidation and filtration, manganese will readily pass through many types of treatment plants. Excess lime softening will remove manganese; however, the common alum coagulation plant used for soft waters generally will not remove manganese unless the pH of the settled water is raised to nine or ten by

lime addition in which case some of the alum floc may pass through the filters and later settle in the distribution system.[3] The common methods used for manganese removal are: (1) oxidation with chlorine or chlorine dioxide; (2) oxidation with ozone; (3) seration through contact-bearing ores;[2] (4) base exchange; (5) the process developed by Zapffe;[4] (6) potassium permanganate treatment; and (7) catalysis.[5] The soluble manganese may be stabilized with polyphosphate which forms complexes tending to remain in solution; however, these complexes often break down in hot water tanks.[2] No single method is the answer to the manganese problem because of many variations of occurrences and water usages.

Little correlation exists between geological manifestations of manganese and iron on the water sheds and their occurrence in rivers, streams, lakes, and underground supplies.[3] Manganese is a detrimental by-product of many large power flood control, and water supply reservoirs and is, therefore, becoming increasingly important in water treatment. A few years after development the hypolimnion of reservoirs may show evidence of manganese even though entering streams show no trace of the element. Quantities of from 0.2 to 20.0 mg/l manganese have been reported in the Tennessee Valley Authority Reservoir discharges.[6] The soluble manganese in lake and river waters containing dissolved oxygen from reaeration and oxygen production of autotrophic plants tends to oxidize to an insoluble precipitate and settle to the bottom muds. During stagnation, anaerobic conditions are produced by the bacterial reduction of settled organic matter, thus creating conditions favoring the reduction of the insoluble oxides of manganese.[7] The manganese

cycle of lakes is very complex and the exact mechanism of manganese reduction is not known.

Very little is known of the identity of the solid oxidized components of manganese in lakes and rivers. Manganese in the untreated water is assumed to be in the manganous state; however, there is no simple effective way to determine the various degrees of oxidation as the water enters the treatment plant, goes through the various treatment devices, and then into the distribution system. Brownley[8] has reported some work on determining the quantity of manganese at various states of oxidation.

The inorganic manganous and ferrous compounds are highly soluble, while the manganic and ferric compounds are relatively insoluble. Manganese exists in freely soluble, bivalent, ionic, manganous form at low pH values and low redox potentials and is generally accompanied by ferrous iron; however, manganous ions may be found in detectable quantities at redox potentials too high to permit the presence of detectable ferrous ions.[9] On oxidation, relatively insoluble hydrated oxides are produced.

Manganese and iron occur as divalent bicarbonates in ground water high in free carbon dioxide, as divalent sulfates in rivers containing acid mine waste waters, and as organic complex matter from swampy areas.[10] Metal working industries may discharge iron and manganese into rivers. Manganese dioxide as pyrolusite is a very common mineral in the more oxidized sedimentary rocks,[9] and the average manganese content of the soils studied by Mann and Quastel[12] was 2,000 to 3,000 parts per million. Anaerobic conditions, low pH, and the presence of carbon dioxide lead to leaching of manganese from soil and rock formations.[11] Evidence of continual bacterial oxidation of manganous to manganic hydroxide has been

shown in soils.[12] However, manganous ions when produced in lakes may persist as such for periods of time in the presence of oxygen under natural stream and lake conditions.

The river and sea muds, examined by Murata,[13] contain 1,000 to 2,000 mg/l manganese and the waters of bottom mud contact layers contained 6 mg/l or more. Murata found that manganese ions exist in an exchangeable form and as insoluble hydrated manganese dioxide minerals of unknown constitution in these river and ocean muds, and that the waters of the contact layers contain dissolved manganese.

Several theories on the mechanism of the reduction of manganese oxides have been advanced by chemists, biochemists, limnologists and others. Observations indicate that temperature is an important factor in the occurrence of this reduction.[14,3] Anaerobisis in a stratified reservoir favors the reduction of manganese oxides.[15,9] Hutchinson[9] and Murata[13] believe that the oxidation-reduction potential, when low, leads to the reduction of manganic to manganous manganese. Goldschmedt,[11] Sherman,[16] and Tanaka[17] are of the opinion that biologically induced changes of pH are an important factor in the manganese cycle. Mann and Quastel[12] indicate that anaerobic bacteria may use manganese dioxide as a terminal hydrogen acceptor. Ingols[15] and Hutchinson[9] believe that hydrogen sulfide can combine with manganese dioxide, forming manganous sulfide which does not precipitate in normal reservoir waters; however, Einsele[7] is of the opinion that hydrogen sulfide is important only as it effects pH. Quastel[18] and Mann[12] have shown that bacterial by-products such as cysteine can reduce manganese dioxide to manganese

monoxide which, on reaction with carbon dioxide, produces soluble manganese carbonate. Purcell[19] believes organic acids may be a factor affecting the reduction of manganese material. Several investigators[18, 12, 19] have shown that carbon dioxide is important in the manganous manganic cycle, and Wiedeman[20] indicates manganese may be reduced by carbon dioxide apart from any biological system.

If all the factors related to the manganese cycle in water were known, the actual mechanism of manganese reduction might be more clearly defined and methods of predicting its occurrence might be developed and possibly its occurrence prevented. This investigation was, therefore, undertaken in an attempt to determine factors related to the changes causing the seasonal occurrence of manganous manganese in natural waters. These factors were to be determined by physical and chemical analysis and observations of a natural water body. To eliminate as many variables as possible, a small unpolluted stream with accessible headwaters was chosen for study.

CHAPTER II

SCOPE OF INVESTIGATION

In nature soluble manganese occurs somewhat seasonally in lakes, reservoirs, rivers, and springs. This study was undertaken to find factors relating to and occurring with the seasonal appearance of manganese. Due to the complexity of the manganese cycle the study was to be confined basically to a small unpolluted spring. A stream near Tucker, Georgia, had been observed for several years. Its rocky bottom became darkened with a black coating during the early spring which cleared up during the fall season. This occurrence was repetitive. On examination of several blackened rocks from the stream bed, the coating proved to contain oxides of iron and manganese; however, the stream waters at that time contained no manganese or iron. The question therefore arose as to what caused the manganese to enter the stream initially, what caused it to precipitate on the rocky bottom, and what caused it to later redissolve from the rocks.

The stream is a part of the Yellow River drainage basin located on the Piedmont Plateau. It is located 1.5 miles southwest of Tucker, Georgia, parallel with Tucker Road. The spring emerges from the ground at several points in a swampy area and flows a half mile down a narrow valley where it is joined by a second stream of comparable size; then it continues a quarter mile to a small lake (Fig. 1). The stream flow varies from 30 to 50 gallons per minute. The joining stream flows at

a rate of 40 to 80 gallons per minute. The stream has considerable fall and the flow is turbulent.

Two springs emerge at the upper end of the stream, one emerges in the creek bed and another emerges at several points in a swampy area and eventually reaches the creek after flowing several hundred feet through swamp marsh. The springs are apparently not from the same immediate source. The main stream flows down a rocky clay bed until it is joined by the second stream, then flows over a sandy rock bottom to the lake.

Since the presence of manganese was apparently seasonal, this study was initiated during the winter season, when no manganese or iron were present, and was continued through the spring and summer seasons, during which the manganese appeared in the spring waters. The following were determined from stream water samples: dissolved oxygen, pH, manganese, iron, alkalinity, carbon dioxide, and temperature. The appearance of the water and creek bed were noted and limited microscopic examinations made. Samples were taken at the springs and at various locations down stream to obtain the pattern of change taking place as the water flowed downstream as well as the seasonal and diurnal variations.

Manganese in solution was expected to appear in the spring water during the spring season and deposit out on the rocky bottom as the water flowed downstream. The mechanism of both the occurrence and oxidation was unknown. Manganous sulfate was added near the springs and the removal of manganese from solution was determined in downstream samples.

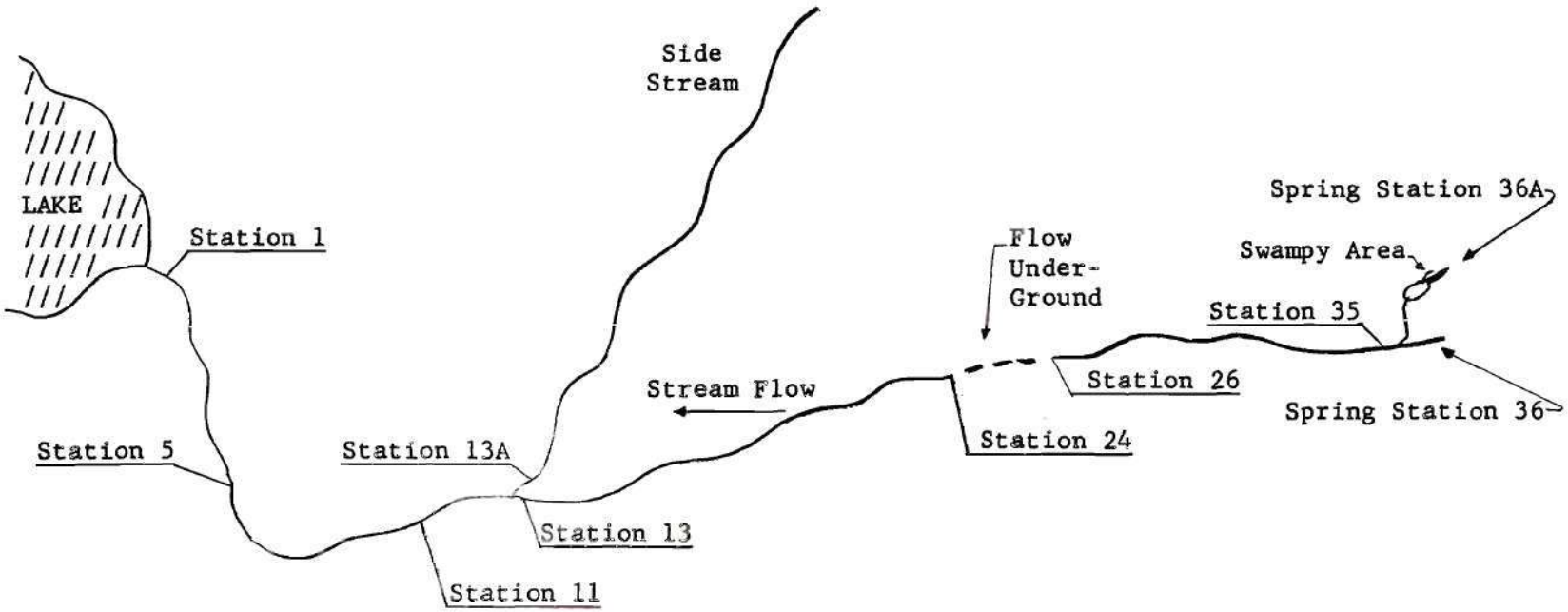

Figure 1. Stream Used in the Investigation
(Station Numbers Set at Even 100-Foot Intervals Above Lake)
No Scale

CHAPTER III

SAMPLING PROCEDURE AND LABORATORY ANALYSIS

Physical and chemical characteristics of the spring water were determined at intervals over a six-month period. A sampling procedure was set up to determine the seasonal variations of stream water quality and the changes of water quality with respect to distance of travel downstream.

The stream was marked off from the lake upstream to the springs in 100-foot stations (Fig. 1). The two springs were designated stations 36 and 36A. All samples were reported according to station numbers. Sampling was started in February at Station No. 1 and additional sampling points added as manganese appeared in the spring water.

The sampling runs were made at intervals which varied from one day to three weeks. All samples were grab samples taken from the flowing portion of the stream. The entire length of the stream was sampled at one time. The data collected for each sample are described below.

Diurnal variations of stream characteristics were determined by collecting ten sets of samples over the entire stream in a 24-hour period. During a 6-hour period manganous sulfate was added to the flowing stream at the springs at a rate of 80 grams per hour. Samples were taken downstream to follow the removal of manganese.

Five-gallon samples of spring water from Station 36 were collected and aerated to determine manganese removal by plain aeration.

A duplicate sample was aerated with iron bacteria obtained from the spring to determine the effect of iron bacteria on the removal of manganese. Samples of the aerated spring water were withdrawn at intervals and analyzed as described below for stream samples.

The date obtained at each sampling point was as follows: time, temperature, dissolved oxygen, pH, manganese, iron, hardness, biochemical oxygen demand (BOD), alkalinity and carbon dioxide. Temperature and dissolved oxygen were measured at the time of sampling and water samples were returned to the laboratory for the remaining analysis. The analytical procedures followed were as given in Standard Method for the Examination of Water, Sewage, and Industrial Wastes, Tenth Edition. Temperature was measured with a calibrated mercury thermometer. The pH was measured with a Beckman glass electrode pH meter, standardized prior to each series of measurements. Dissolved oxygen was determined by the Winkler Method. Manganese was determined by the Persulfate Method using visual color standards. Iron was determined by the Phenanthroline Method using visual color standards. The EDTA Titration Method was used for hardness determination. BOD was determined on undiluted samples with necessary nutrients and seed added according to Standard Methods.

CHAPTER IV

DISCUSSION OF RESULTS

The Two Springs

The two springs, Stations 36 and 36A, emerge from the ground fifty feet apart and at an elevation difference of three feet. The data presented in Figure 2 shows that the springs are not from the same immediate source. The temperature variation was as great as 5°C.; the dissolved oxygen varied as much as 7.0 mg/l; the drop in dissolved oxygen occurred a month earlier at Station 36 than at 36A; the first large increase in iron and manganese occurred one and a half months apart; and iron bacteria were observed at Station 36 a month before their appearance at Station 36A.

The Spring at Station 36

The spring at Station 36 underwent little change through the middle of April. The temperature increased gradually from 10 to 12°C., the dissolved oxygen and pH showed no significant variation and no manganese was found. Iron, which was present throughout April, reached a concentration of 1.0 mg/l on April 16. The iron bacteria Leptothrix ochracea were observed in small quantities at the spring for the first time on April 2. Quantities of ferric hydrate were deposited on the sheaths; however, no detectable manganese was present.

From April 16 to 24, the temperature increased rapidly to 17°C. The concentration of iron increased and manganese appeared for the first

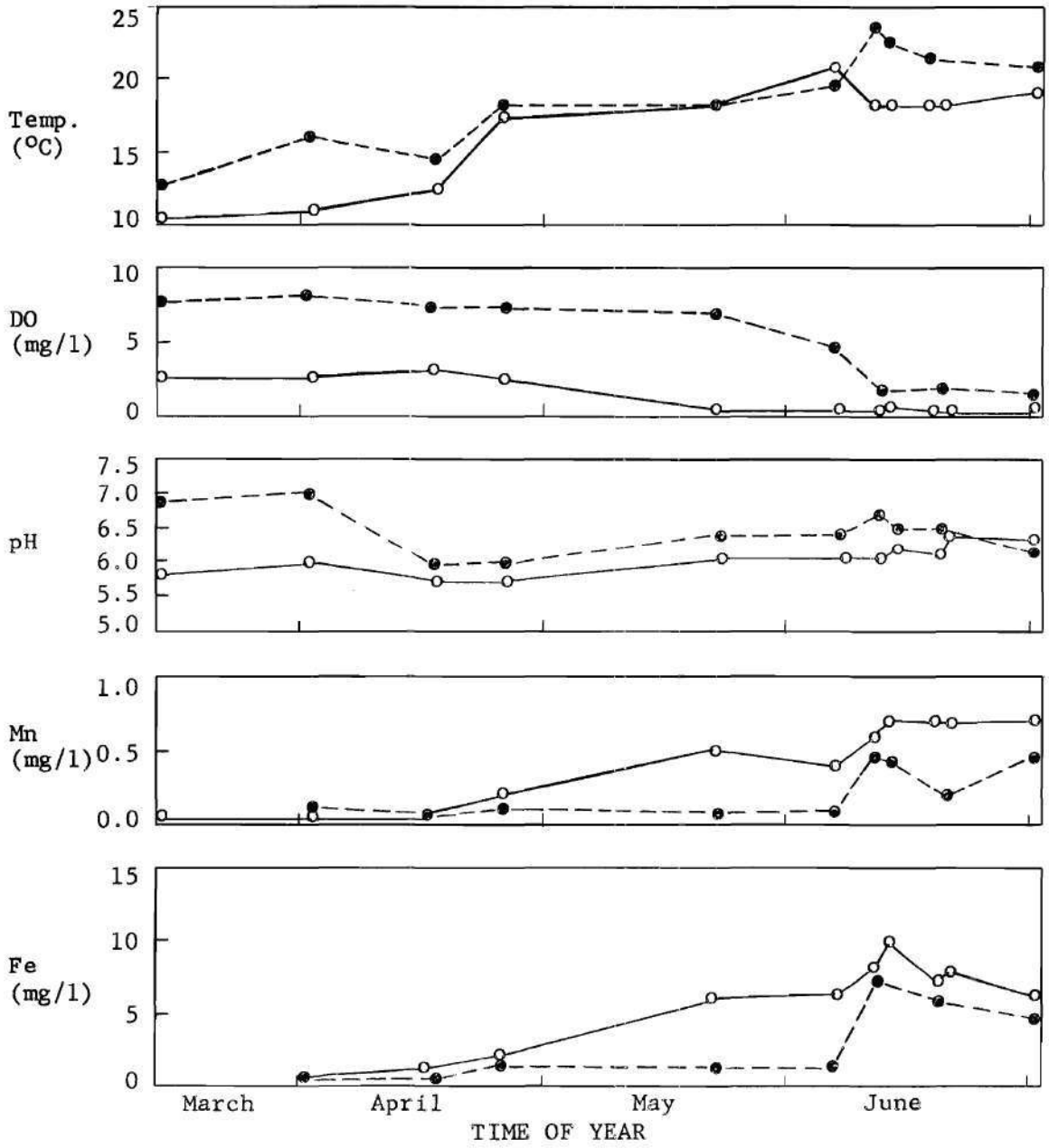

Figure 2. Seasonal Variations of Spring Water Quality

time. Other observed factors remained relatively constant. The pH reached a low point at this time; however, pH changes in this spring were small.

On May 22, large masses of iron bacteria, Leptothrix ochracea, were observed flowing continuously from the spring. The Leptothrix were present in such quantities that the stream sides and bottom were covered for 1,000 feet downstream, where the stream submerged underground for a short distance. The Leptothrix were at this point filtered from the stream water. At the spring the masses of Leptothrix settled out in a dense layer three to four inches thick. Microscopic examination showed all sheaths to contain cells. The deposits on the bacteria sheaths at this time contained manganese as well as iron. The dissolved oxygen in the spring water had been depleted and concentrations of iron and manganese had increased sharply. The pH and temperature showed only a small increase while BOD remained unchanged.

From May 22 to June 5 the observed factors remained relatively constant except for temperature which increased to 21°C. Leptothrix continued to flow from the spring and were present in decreasing quantities along the entire length of the stream and could be observed in the lake water. Unsettled spring water samples, those containing the iron bacteria, had a total iron content in excess of 40 mg/l, while the dissolved iron remained at 6 mg/l.

Both manganese and iron increased sharply between June 5 and 11. The temperature dropped from its June 5 high of 21°C. to 18°C. while other factors remained constant. After June 11, the temperature

gradually increased to 20°C., while the dissolved oxygen, pH and manganese, remained relatively constant. The iron concentration became erratic, varying from 6 to 12 mg/1. Leptothrix continued to flow from the spring; however, empty sheaths were found abundant in July and appeared to increase throughout August. The quantity of iron bacteria flowing from the spring was observed to decrease in late July and August.

The dissolved oxygen reported at Station 36 from May through August varied from 0.0 to 0.7 mg/1. On three occasions throughout this period duplicate samples taken from the pool into which the spring emerges varied by as much as 0.7 mg/1 dissolved oxygen. Samples were also collected by pumping spring water through closed tubing. All samples collected in this manner contained no dissolved oxygen. The spring at Station 36 apparently contained no oxygen after May 22.

BOD samples were collected 100 feet downstream from the springs where dissolved oxygen values were generally greater than 5 mg/1. The BOD values found in these samples were low. The BOD which was observed is believed to be due to organic matter picked up in the stream bed, to inaccuracies in the method used, and to oxidation of dissolved iron.

The Spring at Station 36A

The spring at Station 36A followed a similar pattern to the spring at Station 36, however differed in some respects. The rise of temperature followed the same pattern in both springs although the temperature of the spring at Station 36A remained consistently higher. The pH was somewhat erratic; however, a low point was observed from April 16 to 24

concurrent with the low point observed at Station 36. The BOD remained low in all samples although it was as much as 1.9 mg/l higher than at Station 36. This was believed to be due to the difference in the two stream beds immediately below the springs. The stream bed below Station 36A was a wide swampy area filled with organic debris while that below Station 36 was a narrow clean sandy clay channel.

The dissolved oxygen was in all cases much higher at Station 36A. The drop in dissolved oxygen did not occur until June 5, a month after the drop at Station 36. The dissolved oxygen did not drop to zero but remained at 1.7 to 4.0 mg/l. When dissolved oxygen samples were pumped through closed tubing from the point of emergence of the spring, the dissolved oxygen was not found to be significantly lower than the reported values. It is believed that the spring flows underground for some distance near the ground surface before emerging and that oxygen is dissolved in this region.

Iron and manganese were present in low concentrations until after June 5 when the dissolved oxygen dropped. With the low dissolved oxygen both iron and manganese increased rapidly and remained at high levels.

The iron bacteria, Leptothrix ochracea, were first observed on May 22 in limited numbers. Quantities of both iron and manganese were deposited on the bacterial sheaths. On July 2, large masses of Leptothrix were flowing from the spring and settling out in thick layers along the stream bed. Microscopic examination indicated that all sheaths contained bacterial cells. The quantity of iron bacteria flowing from the spring were observed to decrease in August when empty bacterial sheaths became abundant.

Related Factors

Since the two springs are not from the same immediate source, they may be used for a comparison of factors related to the occurrence of manganese. In both springs iron and manganese follow an almost identical pattern of occurrence. The iron was found before manganese but only in low concentrations. The iron and manganese occurred in a concentration ratio of approximately 10 to 1. This ratio was followed very closely in both springs.

The first appearance of appreciable quantities of iron and manganese followed a rapid increase in temperature and the period of lowest pH. A second rapid increase in temperature is followed by peaks in the iron and manganese concentrations.

The absence of dissolved oxygen shows a very definite relationship to the occurrence of manganese. In each spring the drop of dissolved oxygen to its lowest value is immediately followed by a rapid increase in the concentrations of iron and manganese. The depletion of dissolved oxygen is related to temperature since tree root and bacterial activity in the soil and the consequent utilization of oxygen increased with temperature.

Leptothrix ochracea appeared in limited quantities prior to the depletion of dissolved oxygen. Large masses of Leptothrix began to flow from each spring at a different time although in both cases this occurred a short time after the depletion of dissolved oxygen. The growth of the Leptothrix found in the spring waters before the depletion of dissolved oxygen may have taken place in a zone of oxygen-free

water which became mixed with waters containing dissolved oxygen before the emergence of the spring. It is not known if growth of Leptothrix occurred in the stream bed.

The Stream

Table 1 gives data for Station 1, samples collected above the lake. Samples collected from February 27 to August 9 contained no detectable quantities of manganese with two exceptions where trace quantities were observed. On March 12 trace quantities were found in the spring at Station 36A and were apparently transported to Station 1. On April 24 manganese was found for the first time in all spring waters entering the stream flowing to Station 1 where trace quantities of manganese were again found. No manganese was found at Station 1 in any subsequent samples even though the manganese entering the stream reached concentrations as high as 0.7 mg/l at Station 36 and 13A, and 0.5mg/l at Station 36A

Station 13A, located on a tributary stream immediately above the point of convergence, showed a similar pattern for the occurrence and disappearance of manganese. Trace quantities of manganese were found at Station 13A when it first appeared in the spring water as shown in Table 2. The manganese which persisted in the spring waters was not found at Station 13A on June 10 nor did it recur after June 11.

The manganese was deposited or in some way removed from solution as it flowed down the stream. The mechanism for its removal was not fully operative when the manganese first appeared in the spring waters. Several factors would appear not to be related to the removal of manga-

Table 1. Results of Water Analyses at Station 1

Date	Temperature (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
February 27, 1958	15	9.6	7.1	0		9	1.4	5	0
March 12	14	9.5	7.5	Trace			1.0		
April 2	14	11.2	7.3	0		20	2.5		
April 16	14	8.9	6.6	0	0.5		1.2		
April 24	20	9.7	6.6	Trace	1.0	13	1.9		
May 22	19	8.4	6.9	0	1.0		1.9		
June 5	23	7.9	7.0	0	1.2	15	1.1	18	4
June 10	22	7.1	7.2	0	1.7	15	1.3	20	3
June 11	22	7.6	7.2	0	1.7	16		19	3
June 17	21	7.9	7.1	0	1.5	14	0.9	23	4
July 2	21	8.2	7.2	0	1.3	13		21	3
August 8	21	7.2	7.1	0	1.3		0.3	22	4
August 9	21	7.1	7.0	0	1.0		0 5	22	4

nese. First the dissolved oxygen at Station 1 remained near saturation in all samples. At Station 13A the dissolved oxygen was high in all samples, generally 70 to 80 per cent of saturation. The pH for both stations varied between 6.3 and 7.2 with no evident pattern related to the occurrence of manganese. The BOD, which remained between 0.3 and 2.5 mg/l showed no trend related to the occurrence of manganese. Iron appeared at both stations with the manganese, increased in concentration until June 10 and then showed a gradual decline. The concentration of iron was much lower at Station 1 than at Station 36 which would be expected since iron is readily oxidized in the presence of dissolved oxygen.

The June and July samples were collected to determine the changes in stream characteristics along the entire length of the stream. Figure 3 gives the July 2 results which were typical of all samples during this period. Between 70 and 80 per cent of the iron and manganese was removed from solution and the dissolved oxygen reached 70 per cent saturation within 200 feet of the spring. The temperature and pH did not significantly change in this region. The stream channel was completely covered by Leptothrix from the spring to Station 27. No manganese was found in the stream below Station 29.

On August 8 and 9 the stream was sampled for a 24-hour period to determine the diurnal variation in the stream quality. The results showed that the diurnal variations were very small for all samples and no pattern was apparent in these small variations.

Table 2. Results of Water Analyses at Station 13A

Date	Temperature	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)
April 16	13	7.2	7.1	0		1.4
April 24	20	9.3	6.7	Trace	0.5	1.3
May 22	19	7.8	6.7	0.7	0.8	1.5
June 5	23	6.8	6.8	Trace	2.1	0.8
June 10	22	6.5	6.8	0	1.5	0.6
June 11	21.5	6.9	6.8	Trace	1.4	
June 17	19	6.6	6.4	0	1.2	0.5
June 2	20	6.9	6.3	0	1.0	

Aeration Study

Dissolved iron can be rapidly removed from water by plain aeration; manganese, however, is difficult and slow to oxidize under stream conditions and was not expected to show the rapid removal indicated in Figure 3. Large quantities of manganese were found to deposited on the Leptothrix sheaths.

To determine the effect of Leptothrix on the removal of manganese, samples of the spring water were aerated in the laboratory. Figure 4 shows that plain aeration of a spring water sample containing no Leptothrix did not remove a significant amount of manganese while iron was oxidized very rapidly. Conditions of temperature, dissolved oxygen and

pH followed a pattern similar to that observed in the stream. After 16 hours aeration a large quantity of Leptothrix was added and aeration was continued. The manganese was rapidly removed from solution.

Figure 5 compares two samples aerated simultaneously. The data of both samples is similar except for manganese. The sample containing Leptothrix showed a rapid removal of manganese while the sample of spring water alone had no significant drop in manganese. Although it has been shown that in the presence of Leptothrix manganese is removed from solution rapidly, the mechanism of this removal is not known.

Leptothrix ochracea was observed flowing from the spring in large quantities and settling out along the stream bed; however, it is not known if growth of this organism took place in the stream bed. The manganese was not removed before emerging at the spring because dissolved oxygen was depleted. The removal of manganese in the stream may have been due to a biological mechanism connected with the growth or metabolism of the Leptothrix. An alternate explanation might be that the manganese was oxidized on the bacterial sheaths through a catalytic reaction not connected with the metabolism of the organism itself.

Manganous Sulfate Addition to Stream

During a portion of the 24-hour sampling period on August 8 and 9, manganous sulfate was added to the stream immediately below Station 36. The manganous sulfate was added at a rate of 80 grams per hour. Samples were collected downstream to trace the removal of manganese from the solution. Table 3 shows that manganese was removed from the solution at a high rate even though large quantities of manganese were added to

the stream waters. During the test period the stream channel between Stations 33 and 35 was covered by a thick layer of Leptothrix. No water enters the stream between these stations; therefore, no dilution takes place. The stream was diluted by an approximately equal volume of water before reaching Station 5. The high rate of removal of manganese from solution is apparently due in some way to the presence of Leptothrix.

Table 3. Removal of Manganous Sulfate from the Stream

Station	Manganese at 5:30 P.M.	Manganese at 4:30 P.M.
35	14.0 mg/l	17.0 mg/l
34	8.5 mg/l	12.0 mg/l
33	6.0 mg/l	4.0 mg/l
5	0.1 mg/l	0.3 mg/l

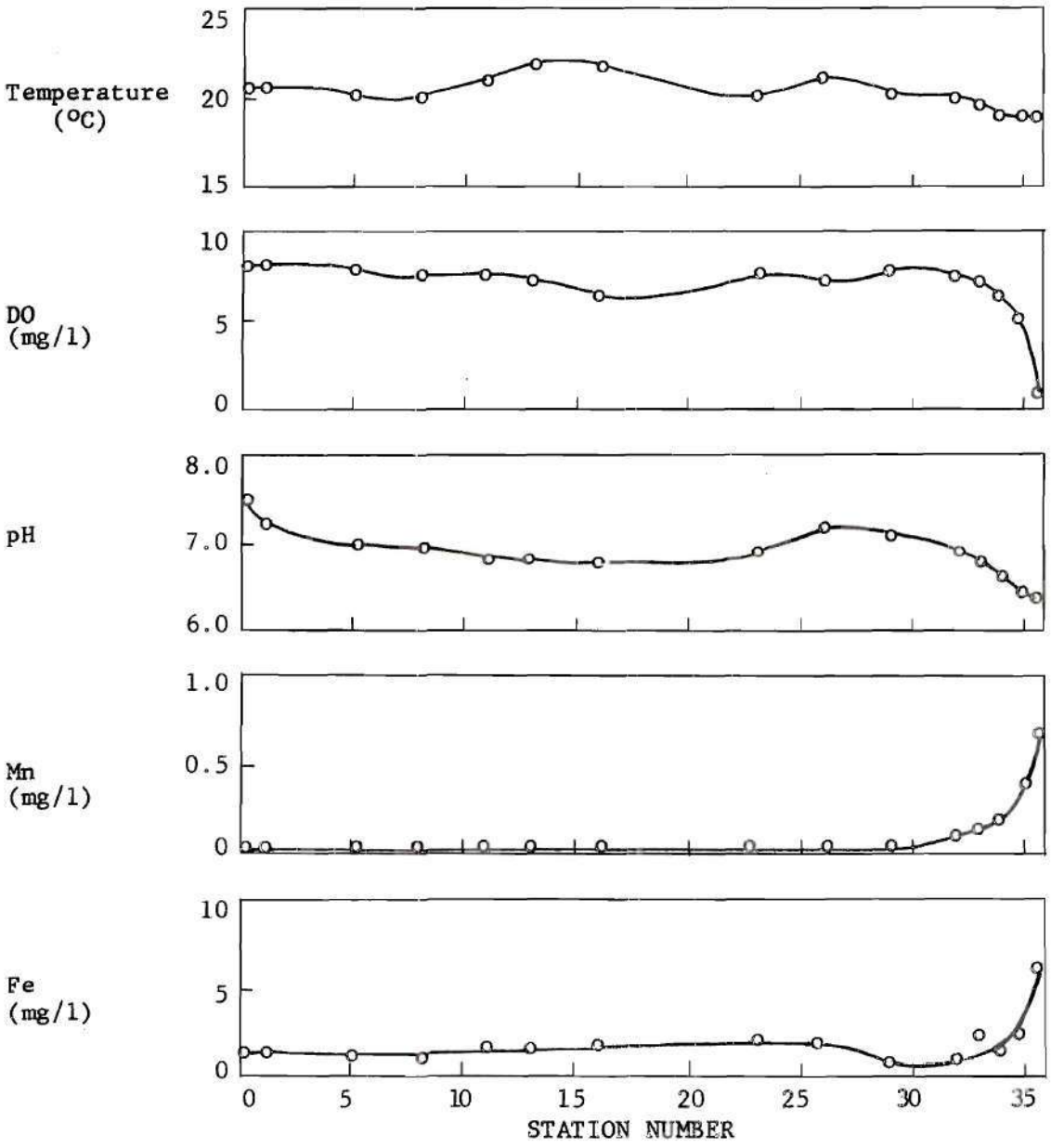

Figure 3. Typical Variation of Stream Characteristics
July 2 Samples

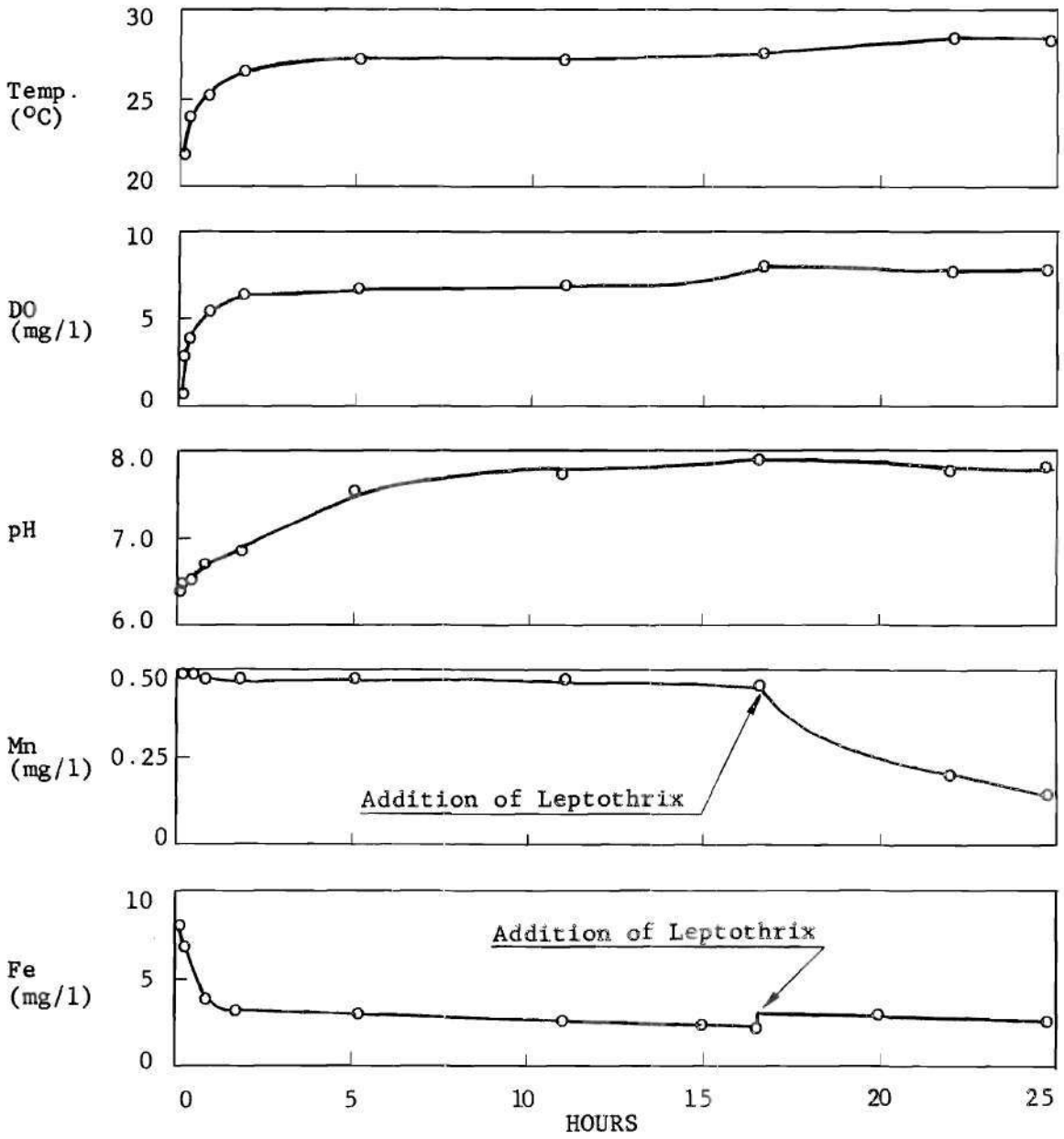

Figure 4. Effect of Aeration on Spring Water Before and After Addition of Leptothrix (Leptothrix Was Added at 16.7 Hours)

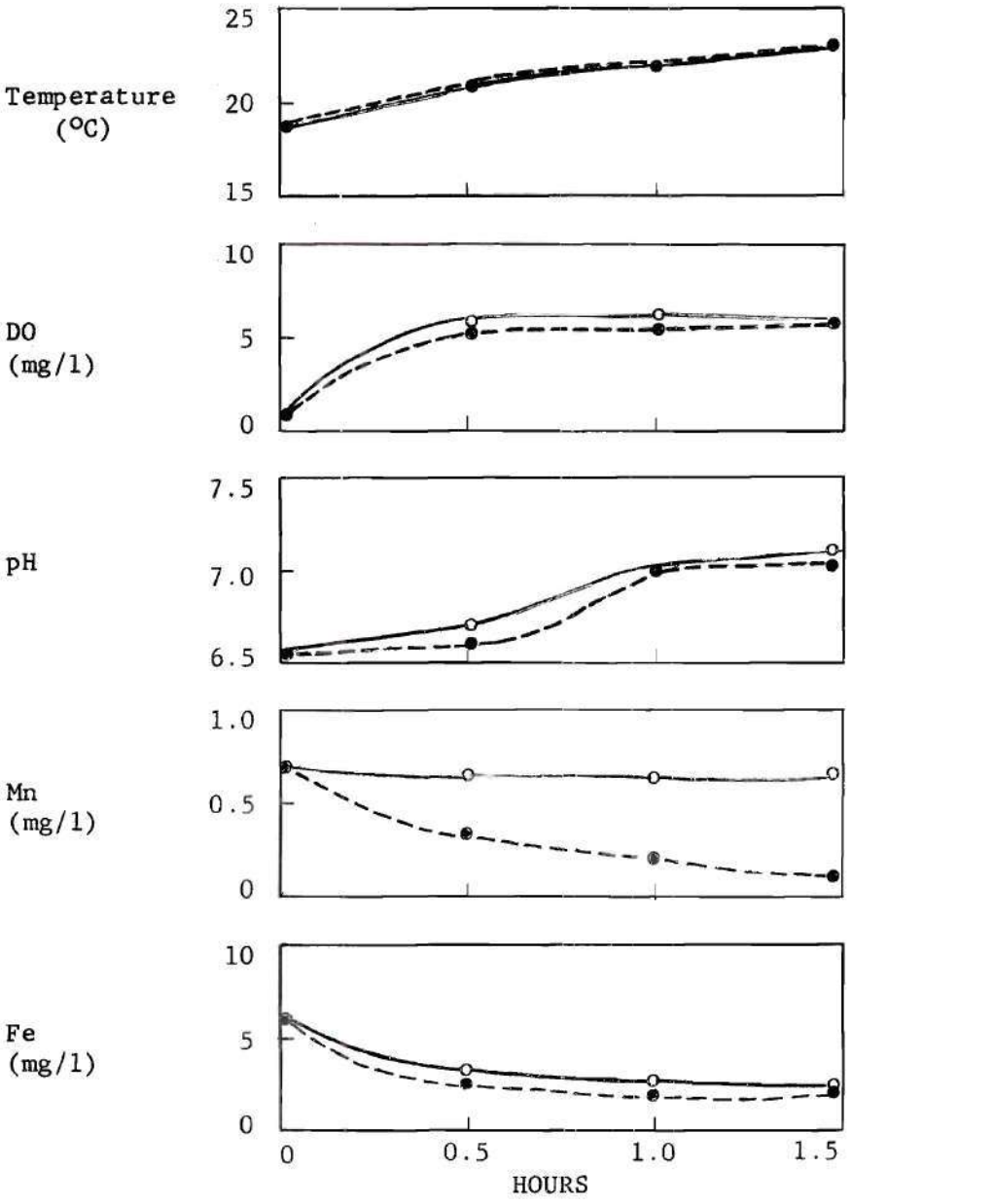

Figure 5. Effect of Aeration on Spring Water in Presence and Absence of Leptothrix

CHAPTER V

CONCLUSIONS

The occurrence of manganese in the natural spring waters observed in this study was related to temperature, dissolved oxygen and iron. Temperature is related to the occurrence of manganese through its effect on biological activity and dissolved oxygen. The absence of dissolved oxygen showed a definite relationship to the presence of high concentrations of manganese, although trace quantities of manganese can be observed before the depletion of dissolved oxygen. The occurrence of iron is related to manganese since conditions favoring the solution of manganese will also favor the solution of iron.

The presence of Leptothrix ochracea in spring waters containing manganese and dissolved oxygen will cause a rapid reduction in the concentration of soluble manganese. The mechanism of this reduction is not known.

Organic material exerting a BOD need not be present for the occurrence of manganese except, possibly, as it is related to the removal of dissolved oxygen.

A P P E N D I X

Results of Analyses on Stream Water Samples

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
Feb. 27, 1958[1]	1	15	9.6	7.1	0		9	1.4	5	0
Mar. 10, 1958[2]	1			2.7	0		20			
Mar. 11, 1958[3]	1			7.1						
Mar. 11, 1958[4]	1			6.9						
Mar. 12, 1958[5]	1	14	9.5	7.5	Trace			1.0		
	36	10	2.5	6.0	0			0.5		
	36A	13	8.0	7.0	Trace			0.7		

1. Day following rain, high flow, reddish-muddy water.

2. The stream flow was average; the water was slightly cloudy (white).

3. Sample taken in the morning.

4. Sample taken at night.

5. Biological sample was completely devoid of protozoa. Sample at station number one contained blue-green algae oscilatoria and colonial bacteria similar to that of activated sludge floc. A dark slime was found on the rocky bottom; this slime contained no manganese. The stream flow was average.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
April 2, 1958[6]	1	14	11.2	7.3	0		20	2.5		
	36	11	2.5	6.1	0	____[7]	0	0.2		
	36A	16	8.3	7.1	Trace		16	1.2		
April 16, 1958[8]	1	14	8.9	6.6	0	0.5		1.2		
	13A	13	7.2	7.1	0			1.4		
	22	14	7.5	6.3	0			0.2		
	36	12	3.2	5.8	0	1.0		0.0		
	36A	14	7.5	6.1	0	0.7		0.3		

6. The stream flow was average. The water from Station Number One contained protozoa, rotifers, green algae, and blue-green algae.

7. The spring water of Station Number 36 contained Leptothrix ochracea, which had quantities of ferric hydrate deposited on the sheaths. Nearly all sheaths contained the bacteria cells.

8. Day following rain, high flow, water slightly turbid.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
April 24, 1958[9]	1	20	9.7	6.6	Trace	1.0	13	1.9		
	13A	20	9.3	6.7	Trace	0.5		1.3		
	36	17	2.5	5.9	0.2	2.0		0.0		
	36A	18	7.5	6.1	0.1	1.5		1.2		
May 22, 1958[10]	1	19	8.4	6.9	0	1.0		1.9		
	13A	19	7.8	6.7	0.7	0.8		1.5		
	36	18	0.1	6.1	0.5	6.0[11]		0.0		

9. The stream flow was slightly below average.

10. The stream flow was slightly below average.

11. Masses of iron bacteria, Leptothrix ochracea, were flowing out of the spring and covering the sides and bottom of the stream bed for several hundred feet, until the stream went underground at Station Number 26. At the spring the masses of bacteria were 3 to 4 inches thick as a light floc, reddish brown in color.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
May 22, 1958[10]	36A	18	7.2	6.5	Trace	1.3		1.9		
June 1, 1958[12]										
June 5, 1958[13]	1	23	7.9	7.0	0	1.2	15	1.1	18	4
	11	23	7.0	7.2	Trace	2.5	14	1.0		
	13	23	6.2	7.3	Trace	2.5	14	1.1		
	13A	23	6.8	6.8	Trace	2.1	20	0.8		
	33	21	6.6	6.7	0.3	2.3	20	0.1		
	36	20	0.7	6.1	0.4	6.0[14]	22	0.2	30	40

10. The stream flow was slightly below average.

12. Iron bacteria were reported on the lake surface.

13. The stream flow was slightly below average. Iron bacteria were deposited on the stream bed from Station Number 36 to the lake in decreasing quantities.

14. The dissolved iron was 6.0 ppm; the total iron, which would include the iron deposited on the sheaths of the iron bacteria which were flowing from the spring, was greater than 40 ppm.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
June 5, 1958[13]	36A	19	5.0	6.5	0.1	1.7	15	0.9		
June 10, 1958[15]	1	22.5	7.1	7.2	0	1.7	15	1.3	20	3
	5	22	7.0	7.2	0	2.0	16	1.0		
	11	22.5	6.8	7.2	0	2.4	14	0.7		
	13	22.5	6.5	6.9	Trace	2.7	17	0.8		
	13A	22	6.5	6.8	0	1.5	10	0.6		
	15.5	22.5	5.3	6.9	Trace	3.0	19	0.6		
	18	22.5	6.0	7.1	Trace	5.8	21	0.4		
	22	20.5	7.2	7.2	Trace	3.2	22	0.5		

13. The stream flow was slightly below average. Iron bacteria were deposited on the stream bed from Station Number 36 to the lake in decreasing quantities.

15. Kjeldahl Nitrogen Tests were run on samples from Station 13 and 30. In both samples the Kjeldahl Nitrogen was found to be zero.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
June 10, 1958[15]	26	20.5	7.1	7.3	Trace	1.2	23	0.7		
	30	19.5	7.2	7.0	0.15	1.5	22	0.6		
	33	19	6.1	6.8	0.25	2.0	21	0.1		
	36	18	0.1	6.2	0.60	8.5	26		37	45
	36A	23.5	2.0	6.8	0.50	7.0	21	0.6		
June 11, 1958[16]	1	22.5	7.6	7.2	0	1.7	16		19	3
	5	22.5	7.5	7.2	0	1.9				
	11	22.5	7.3	7.1	0	2.2				
	13	22.5	7.0	6.9	0	2.4				

15. Kjeldahl Nitrogen Tests were run on samples from Stations 13 and 30. In both samples the Kjeldahl Nitrogen was found to be zero.

16. The stream flow was slightly below average.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
June 11, 1958[16]	13A	21.5	6.9	6.8	Trace	1.4				
	15	22	5.8	6.8	Trace	3.2				
	18	21.5	6.2	7.0	Trace	4.0				
	22	21.5	7.4	7.1	Trace	2.8				
	27	21.5	7.4	7.2	0.07	0.7				
	30	20	7.3	7.0	0.13					
	33	20.5	6.2	6.9	0.24	3.5				
	35	19	5.8	6.8	0.26	7.0				
	36	18	0.5	6.3	0.70	10.0	28		41	40
	36A	22.5		6.6	0.45					
June 17, 1958[16]	1	20.5	7.9	7.1	0	1.5	14	0.9	23	4

16. The stream flow was slightly below average.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
June 17, 1958[17]	5	20.5	7.8	7.1	0	1.5		0.5		
	11	20	6.4	6.3	0	1.5		0.3		
	13	22	6.8	7.0	0	2.0		0.3		
	13A	19	6.6	6.4	0	1.2		0.5		
	30	19.5	6.7	6.8	0.07	1.5		0.2		
	31.5	19	6.5	6.7	0.12	2.0		0.4		
	33	19	5.8	6.6	0.28	1.5		0.2		
	33.7	20.5	5.0	6.5	0.33	2.5		0.3		
	34.5	20	4.6	6.0	0.32	3.2		0.5		
	35	20	3.5	6.1	0.45	4.0		0.3		
	36	18.5	0.1	6.2	0.70	7.0	25		43	53
	36A	21	2.2	6.6	0.20	6.0				

17. The stream flow was slightly below average.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
June 18, 1958[18]	36	18.5	0.2	6.5	0.7	8.0				
July 2, 1958	0	20.5	8.2	7.5	0	1.3				
	1	20.5	8.2	7.2	0	1.3	13		21	3
	5	20	7.9	7.0	0	1.0				
	8	20	7.8	7.0	0	1.0				
	11	21	7.6	6.9	0	1.5				
	13	22	7.5	6.8	0	1.7				
	13A	20	6.9	6.3	0	1.0				
	16	21.5	6.1	6.8	0	1.7				
	23	20	7.8	6.9	0	2.1				
	26	21	7.3	7.2	0	1.9				
	29	20	7.8	7.1	0	0.7				

18. The stream flow was slightly below average.

Results of Analyses on Stream Water Samples (Continued)

Date	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Hardness as $CaCO_3$ (mg/l)	BOD (mg/l)	Alk as $CaCO_3$ (mg/l)	CO_2 (mg/l)
July 2, 1958	32	20	7.6	6.9	0.10	0.9				
	33	19.5	7.2	6.8	0.15	2.3				
	34	19	6.3	6.6	0.2	1.5				
	35	19	5.3	6.4	0.40	2.5				
	36	19	0.7	6.4	0.70	6.0	23		46	39
	36A	20.5	1.7	6.2	0.50	5.0				
July 18, 1958	36	20	0.1	6.4	0.70	9.0	26		50	40

Results of Water Analyses on Twenty-Four Hour Sampling Run

Date	Time	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)	Alkalinity Phen (mg/l)	Alkalinity Methol (mg/l)	CO_2 (mg/l)
August 8, 1958	19:30	5	21	7.2	7.1	0.00	1.3	0.3	0	22	4
		34	21	5.2	6.7	0.20		0.0	0	26	11
		35	21.5	5.0	6.6	0.35	5.0	0.6	0	26	15
		36	20	0.0	6.3	0.58	13.0		0	58	60
		36A	22	4.0	6.7	0.35	6.0	1.0	0	26	11
	21:15	5	21	7.1	7.1	0.00	1.3	0.3	0	22	4
		34	21	5.4	6.7	0.25	6.6	0.6	0	28	12
		35	21.5	4.8	6.7	0.35	10.0	0.4	0	28	12
		36	20	0.0	6.4	0.60	12.0		0	54	45
		36A	22	4.1	6.8	0.25	7.0	1.0	0	30	10
	23:00	5	21	7.2	7.2	0.00	1.3	0.4	0	22	3
		34	21	5.5	6.7	0.20	4.5	0.4	0	24	10
		35	21.5	4.8	6.6	0.30	8.0	0.8	0	30	15

Results of Water Analyses on Twenty-Four Hour Sampling Run (Continued)

Date	Time	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)	Alkalinity Phen (mg/l)	Alkalinity Methol (mg/l)	CO_2 (mg/l)
August 8, 1958	23:00	36	20	0.0	6.3	0.55	12.0		0	54	55
		36A	22	4.2	6.7	0.25	7.0	0.8	0	32	13
August 9, 1958	0:15	5	21	7.2	7.2	0.05	1.0	0.4	0	23	3
		34	21	5.4	6.8	0.45	2.5	0.1	0	26	8
		35	21	4.8	6.7	0.50	3.2	0.6	0	32	13
		36	20.5	0.1	6.3	0.60	14.0		0	52	55
		36A	21.5	4.5	6.9	0.40	4.0	1.2	0	30	8
	6:30	5	21	7.2	7.1	0.00	1.1	0.4	0	22	4
		33	21	6.4	6.7	0.55	1.5	0.2	0	24	10
		34	21	5.6	6.6	0.45	2.5	0.5	0	26	15
		35	21	5.5	6.6		3.8	0.8	0	28	15
		36	20	0.0	6.2	0.60	10.0		0	52	70
		36A	21.5	4.7	6.7	0.55	5.5	1.0	0	28	11

Results of Water Analyses on Twenty-Four Hour Sampling Run (Continued)

Date	Time	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)	Alkalinity Phen (mg/l)	Alkalinity Methol (mg/l)	CO_2 (mg/l)
August 9, 1958	8:30	5	21	7.7	7.1	0.10	1.2	0.6	0	22	4
		33	20.5	6.5	6.8	0.20	1.7	0.4	0	26	8
		34	21	5.7	6.6	0.30	2.3	0.3	0	28	15
		35	21	5.3	6.6	0.35	4.3	0.5	0	28	15
		36	20	0.0	6.2	0.60	14.0		0	52	70
		36A	21.5	4.6	6.7	0.35	5.0	0.7	0	26	11
	10:30	5	21.5	7.4	7.1	0.10	1.0	0.5	0	22	4
		33	21.5	6.4	6.7	0.35	1.5	0.4	0	26	11
		34	21.5	5.4	6.6	0.35	2.5	0.5	0	26	15
		35	21.5	5.1	6.5	0.40	4.0	0.3	0	30	20
		36[1]	20.5	0.6	6.2	0.55	10.0		0	44	55
		36A	22	4.9	6.6	0.35	4.0	1.0	0	28	15

1. This sample taken at a different point of outflow.

Results of Water Analyses on Twenty-Four Hour Sampling Run (Continued)

Date	Time	Station	Temp (°C)	DO (mg/l)	ph	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)	Alkalinity Phen (mg/l)	Alkalinity Methol (mg/l)	CO_2 (mg/l)
August 9, 1958	11:00[2]										
	13:30	5	22	7.2	7.0	0.15	0.8	0.4	0	22	4
		33	21.5	6.4	6.8	6.0	3.0	0.4	0	26	8
		34	21.5	5.3	6.7	8.5	2.5	0.3	0	26	11
		35	21.5	4.7	6.6	14.0	2.5	0.3	0	28	15
		36	20	0.0	6.3	0.75	12.0		0	50	55
		36A	23	3.6	6.8	0.40	9.0	1.1	0	28	9
	16:30	5	22	7.1	7.0	0.35	1.0	0.5	0	22	4
		33	21.5	6.4	6.8	4.0	1.5	0.3	0	22	7
		34	21.5	5.2	6.7	12.0	1.5	0.6	0	30	12

2. Addition of Manganous Sulfate ($MnSO_4$) was started just below Station 36 at a rate of 80 grams per hour for a six-hour period.

Results of Water Analyses on Twenty-Four Hour Sampling Run (Continued)

Date	Time	Station	Temp (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	BOD (mg/l)	Alkalinity Phen (mg/l)	Alkalinity Methol (mg/l)	CO_2 (mg/l)
August 9, 1958	16:30	35	21.5	4.5	6.6	17.0	3.2	0.7	0	30	15
		36	20	0.0	6.4	5.3[1]	13.0		0	50	40
		36A	23	2.4	6.7	0.4	5.0	1.8	0	34	15
	19:30	5	21	7.2	7.0	0.0[2]	0.8	0.5	0	22	4
		33	21.5	6.4	6.7	3.2[2]	1.0	0.2	0	24	10
		34	21	5.2	6.6	3.5[2]	2.3	0.0	0	26	15
		35	21.5	4.6	6.5	6.0[2]	4.0	0.5	0	28	20
		36	20.5	0.0	6.3	2.4[1]	12.0		0	52	55
		36A	23	3.0	6.7	0.4	5.0	1.3	0	26	10

1. Manganese from the Manganese Sulfate may have contaminated this sample since its point of addition was very close to Station 36.

2. Manganous Sulfate addition stopped at 17:00.

Manganese Removal by Aeration

Before and After Addition of Leptothrix[1]

Time of Aeration (Hours)	Temperature (°C)	DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)
0.00	22	0.7	6.4	0.50	8.0
0.17	22	3.0	6.5	0.50	8.0
0.33	24	3.9	6.5	0.50	7.0
0.83	25.2	5.6	6.7	0.48	4.0
1.83	26.5	6.6	6.8	0.48	3.0
5.16	27	6.9	7.6	0.47	3.0
11.00	27	7.0	7.7	0.46	2.5
16.66	27.5	7.1	7.9	0.46	2.0
16.70[2]					
22.00	28.5	6.7	7.7	0.20	3.0
73.50	29.5	6.9	7.8	0.10	2.5
100.30	29.5	7.0	7.9	0.05	2.0

1. Spring water samples taken from Station 36 on June 18, 1958.

2. Following the sampling at 16.66 hours, iron bacteria were added to the aeration jar, approximately one liter as settled undisturbed from the spring water.

Manganese Removal by Aeration of Settled Spring Water

and Spring Water Containing Leptothrix[1]

Aeration Time (Hours)	Temperature	Settled Spring Water DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)	Spring Water Containing Leptorhrix DO (mg/l)	pH	Mn (mg/l)	Fe (mg/l)
0.0	19	0.9	6.5	.70	6.0	0.9	6.5	.70	6.0
0.5	21	6.9	6.7	.65	3.0	6.8	6.6	.35	2.5
1.0	22	7.0	7.0	.65	2.5	6.9	7.0	.20	2.0
1.5	23	7.0	7.1	.65	2.0	7.0	7.0	.10	2.0

1. Spring water samples taken from Station 36, July 2.

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